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The influence of HCl on SO_2 absorption in the spray dry scrubbing process

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Abstract

To examine the influence of HCl on SO_2 removal in the spray dry scrubbing process, preliminary experiments on the effect of adding $CaCl_2$ to the lime slurry on SO_2 absorption efficiency were performed in a laboratory scale spray dryer. It was found that the SO_2 removal efficiency is augmented at $CaCl_2$ concentrations up to 1.2 g/l in the lime slurry. This is ascribed to the influence of the prolonged drying process. However, SO_2 absorption efficiency cannot be improved further at higher $CaCl_2$ concentrations. A simple estimation shows that this cannot be ascribed solely to the influence of the drying behavior of the droplets and more complex explanations have to be found. Subsequently, experiments on the simultaneous absorption of SO_2 and HCl were performed. It was found that the SO_2 removal efficiency is enhanced at low HCl concentrations in the flue gas. This is ascribed to the formation of $CaCl_2$ in the droplets, resulting in a prolonged drying process. After reaching a maximum, the SO_2 removal efficiency falls again at higher HCl concentrations. This can be explained with the competing absorption process in which HCl is thermodynamically favored. © 2002 Published by Elsevier Science B.V.

Keywords: Spray dry scrubbing; Absorption; Sulfur dioxide; Hydrogen chloride; Hydrated lime

1. Introduction

In many incineration processes, especially in waste incineration, the resulting flue gas contains acid components such as sulfur dioxide (SO_2) and hydrogen chloride (HCl) which have to be removed to meet environmental standards. Spray dry scrubbing is a commonly used process to achieve this. A fine spray of lime slurry is dispersed concurrently into the flue gas stream. The acid gas components absorb in the droplets and react with the hydrated lime ($Ca(OH)_2$) to form salts according to the following overall reaction equations:

$$SO_2 + Ca(OH)_2 \rightarrow CaSO_3 \cdot \tfrac{1}{2}H_2O + \tfrac{1}{2}H_2O \qquad (1)$$

$$2HCl + Ca(OH)_2 \rightarrow CaCl_2 \cdot 2H_2O \qquad (2)$$

At the same time the water evaporates from the droplets and a dry, powdery product results. This is usually separated from the cleaned flue gas by bag filters or electric precipitators. The product consists of the reaction products and unreacted $Ca(OH)_2$. To obtain a high absorption efficiency, an excess of $Ca(OH)_2$ is required. Consequently the conversion of $Ca(OH)_2$ is incomplete.

The removal of SO_2 with spray dry absorption has been extensively studied and modeled [1,2]. It was shown that the drying conditions greatly influence the absorption process. The harsher the drying conditions, the less time is available for absorption on the wet surface, the lower is the resulting removal efficiency.

The removal of HCl and the simultaneous removal of SO_2 and HCl has not been studied as extensively. Only few references are to be found in literature [3,4]. For the simultaneous removal of SO_2 and HCl two competing effects can be expected:

- While reaction of hydrated lime with sulfur dioxide produces calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2H_2O$) (Eq. (1)), which has a very low solubility in water, the reaction with HCl produces calcium chloride ($CaCl_2$), a salt with a very high solubility. Consequently, $CaCl_2$ lowers the vapor pressure of the water in the droplets and thereby significantly prolongs the drying process, enhancing the removal of SO_2.
- Since the absorption of HCl on the droplets is thermodynamically favored, it supersedes the absorption of SO_2 at high HCl concentrations.

To examine the first phenomena, experiments were performed in which $CaCl_2$ was added to the lime slurry, thus simulating completed HCl absorption and reaction within the droplet had already taken place. Subsequently experiments on the simultaneous removal of SO_2 and HCl were performed.

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Nomenclature

C	concentration (mol/m)
N	molar flow (mol/s)
Pe'	Peclet number (–)
R	droplet radius (m)
t	time (s)
T	temperature (°C)
U	calcium hydroxide conversion (–)
y	fraction (–)
Y	load

Greek symbols

δ	binary diffusion coefficient (–)
η	removal efficiency (–)
λ	stoichiometric ratio (–)
ν	stoichiometric factor (–)

Subscripts

i	component
in	at spray dryer inlet
out	at spray dryer outlet
ov	overall
surf	droplet surface
sus	suspension
0	initial value

Superscripts

$\sim$	molar
–	average

2. Experimental set-up

The experimental set-up is shown in Fig. 1. The experiments are performed in a laboratory scale spray dryer of 0.16 m diameter and 1.5 m length. Heated ambient air, steam and SO_2 and/or HCl gas streams are mixed in a static mixer and introduced into the spray dryer as artificial flue gas. The mass flow of ambient air is measured by an orifice flow meter and was kept constant at 16 m^3/h. The HCl and SO_2 gas streams are each controlled by mass flow controllers. The artificial flue gas is evenly distributed over the spray dryer by a perforated plate at the inlet. The lime slurry is taken from a stirred tank and fed by a peristaltic pump into the two fluid nozzle where it is atomized by compressed air. At the outlet of the spray dry scrubber the dry product is separated from the gas stream by a cyclone. The temperatures at the inlet and outlet of the spray dryer are determined with thermocouples. After leaving the measuring section the gas is cleaned by a wet scrubber to remove any remaining acid gas components. The process parameters used in this work are given in Table 1. The SO_2, HCl and H_2O concentrations are measured by an infrared photometer (MCS100 HW, Perkin Elmer) at the inlet of the spray dryer and at the outlet, after the cyclone. Measurements were only taken at steady state. During an experimental run only the concentration of SO_2 was varied while all other process parameters were kept constant. This was done in order not do disturb the drying conditions within the spray dryer.

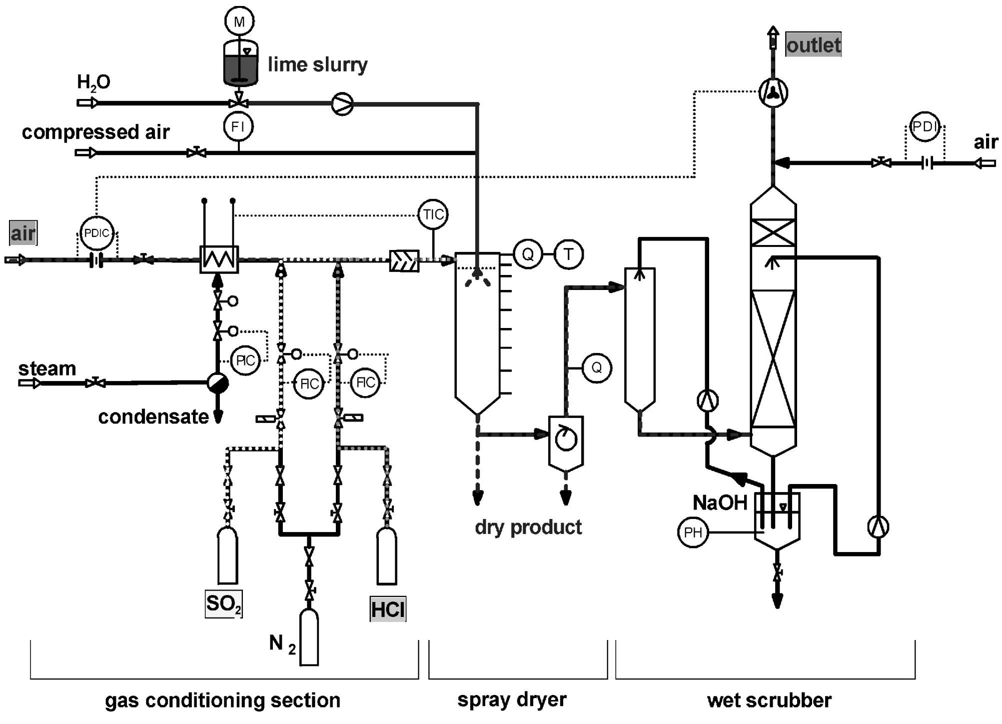

Fig. 1. Experimental set-up.

Table 1
Process parameters

Flue gas	
Mass flow of dry air (kg/s)	5.6×10^{-3}
Inlet temperature (°C)	200–250
HCl concentration (ppm)	0–2000
SO_2 concentration (ppm)	0–2000
Water vapor mole fraction (–)	0.10
Lime slurry	
Mass flow (kg/s)	8.3×10^{-5}–25×10^{-5}
Lime weight fraction (–)	0.025–0.15
Initial $CaCl_2$ weight fraction (–)	0–0.03
Spray nozzle	
Mass flow of dry air (kg/s)	4.0×10^{-4}

3. Results and discussion

3.1. Definitions

The experimental results are discussed in terms of stoichiometric ratio and absorption efficiency. The absorption efficiency is defined as the ratio of the mole flux of acid gas component removed in the spray dryer to the mole flux of the component at the inlet of the spray dryer

$$\eta_i \equiv \frac{N_{i,in} - N_{i,out}}{N_{i,in}} \tag{3}$$

The stoichiometric ratio can be defined with respect to one acid gas component as the ratio of calcium hydroxide mole flux to the mole flux of the acid gas component multiplied with the stoichiometric factor:

$$\lambda_i \equiv \frac{\dot{N}_{Ca(OH)_2,in}}{\nu_i \dot{N}_{i,in}} \tag{4}$$

In accordance with Eqs. (1) and (2) the stoichiometric factors for SO_2 and HCl are 1 and 0.5, respectively. The overall stoichiometric ratio is defined as the ratio of the mole flux of calcium hydroxide to the total stoichiometric equivalent of acid gas components. This is a parameter of industrial relevance and is defined as

$$\lambda_{ov} \equiv \frac{\dot{N}_{Ca(OH)_2,in}}{\dot{N}_{SO_2,in} + 0.5\dot{N}_{HCl,in}} \tag{5}$$

The conversion efficiency of calcium hydroxide is defined as the ratio of the mole flux of converted calcium hydroxide to the mole flux at the inlet of the spray dryer and is related to the stoichiometric ratio and removal efficiency as follows:

$$U_{Ca(OH)_2} \equiv \frac{N_{Ca(OH)_2,in} - N_{Ca(OH)_2,out}}{N_{Ca(OH)_2,in}} = \frac{\eta_{HCl}}{\lambda_{HCl}} + \frac{\eta_{SO_2}}{\lambda_{SO_2}} \tag{6}$$

3.2. The effect of $CaCl_2$ on SO_2 removal

To examine the influence of $CaCl_2$ as the reaction product of HCl absorption on SO_2 removal, $CaCl_2$ was added to the lime slurry used in spray dry absorption.

Generally, additives to the lime slurry can influence the absorption efficiency in several ways:

- By influencing the drying behavior of the droplets. This pertains especially to hygroscopic additives like $CaCl_2$ which prolong the drying process and therefore enhance the absorption efficiency.
- By influencing the thermodynamic behavior of the reaction components. In our case this could mean an altered absorption of SO_2 or a change in the dissolution rate or solubility of the $Ca(OH)_2$ particles within the droplet.
- By increasing the alkalinity of the sorbent droplets. With $CaCl_2$ as a neutral salt this is not the case.
- By changing the surface area of the dried particle. As stated by Hill and Zank [2], the reaction of SO_2 with the dried product is of negligible significance to the absorption efficiency within the spray dryer. Consequently, the surface area of the dried product should have no influence on the absorption efficiency.

The experimental results are shown in Fig. 2. The diagonal line on the left indicates the theoretical limit of total $Ca(OH)_2$ conversion. The results show that adding up to 1.2 wt.% $CaCl_2$ to the lime slurry enhances the removal efficiency of SO_2 over the whole stoichiometric range. Above 1.2 wt.% however, no further improvement of the removal efficiency can be achieved by adding more $CaCl_2$. Similar results have been obtained by Wang [5]. These authors examined the influence of several hygroscopic additives in spray dryer flue gas desulfurization.

The enhancement of SO_2 removal at low initial $CaCl_2$ concentrations can be attributed to the prolonged drying process, which occurs as a result of the lowering of the water activity in the droplet and consequently of the water vapor pressure at the droplet surface. Furthermore, $CaCl_2$ slightly enhances the absorption equilibrium of SO_2 in water [6]. However, this was only examined for $CaCl_2$ molalities up to 0.5 mol/kg. In our case, the concentration of $CaCl_2$ in the droplet ranges up to saturation (about $14\,\mathrm{mol/kg_{H_2O}}$ at 100 °C). The influence of $CaCl_2$ on $Ca(OH)_2$ solubility or dissolution rate has not yet been examined in literature.

However, it has been claimed that the presence of $CaCl_2$ and $Ca(OH)_2$ in the droplet leads to the formation of an alkaline salt complex $Ca(OH)_2 \cdot CaCl_2 \cdot H_2O$ with a weaker affinity for water [5]. According to these authors this explains the fact that SO_2 absorption cannot be further enhanced at higher $CaCl_2$ concentrations.

In order to investigate how the initial $CaCl_2$ concentration affects the overall drying rate of the droplets and therefore the absorption of SO_2 a rough estimation was carried out: It was examined, how fast the saturation concentration at the droplet surface is reached during the drying process and the loss of mass up to this point. Since drying after reaching saturation on the surface is very slow, there should be an initial concentration of $CaCl_2$ above which the overall drying time becomes independent of the initial concentration. The concentration of the salt at the droplet surface can be

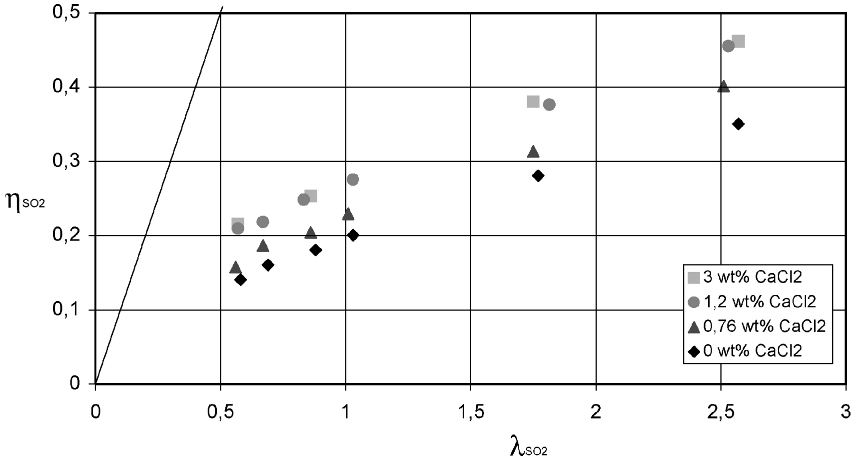

Fig. 2. Influence of initial $CaCl_2$ concentration in the lime slurry on SO_2 removal efficiency. Process parameters: $T_{in} = 200\,°C$, $\%y_{H_2O} = 0.1$, $y_{sus,Ca(OH)_2} = 10\,wt.\%$.

estimated for the initial stage by the following equation [7]:

$$C_{CaCl_2,surf} = C_{CaCl_2,0}\left(\frac{1}{2}\left(1+\frac{2}{\sqrt{\pi}}\right)Pe'\sqrt{\frac{\delta t}{\bar{R}^2}+1}\right) \qquad (7)$$

with the Peclet number

$$Pe' = \frac{\bar{R}(d\bar{R}/dt)}{\delta_{CaCl_2,H_2O}} \qquad (8)$$

Since only the initial stage of the drying process is of interest, the radius of the droplet and the shrinking velocity can be averaged.

By this, the time needed for the droplet surface to reach saturation can be calculated and compared to a calculated drying time of the remaining droplet, the vapor pressure of which is lowered to the minimum. With this, the influence of the initial concentration of $CaCl_2$ on the overall drying time was estimated.

Fig. 3 shows the calculated overall drying time scaled with the drying time for a droplet at saturation concentration with respect to the initial $CaCl_2$ concentration. This was calculated for the best case with respect to the assumptions (i.e. high average drying rate in the initial stage, slow

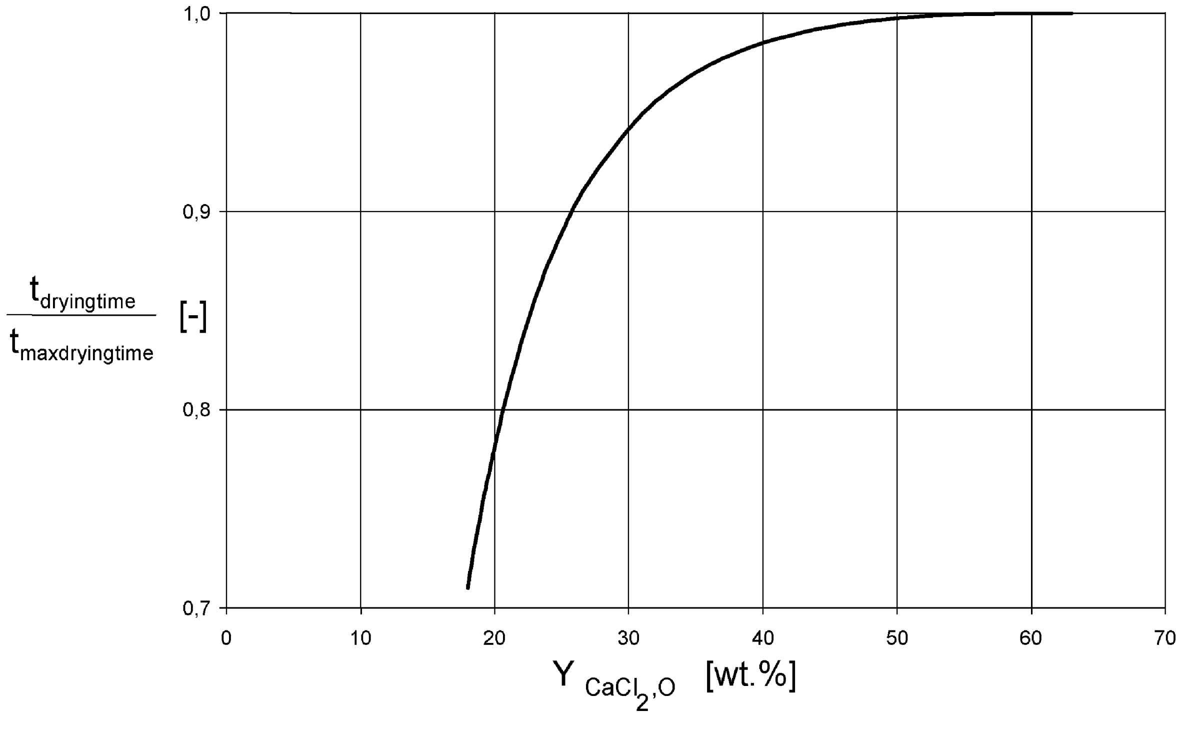

Fig. 3. Estimation of drying time with respect to initial $CaCl_2$ concentration in the lime slurry.

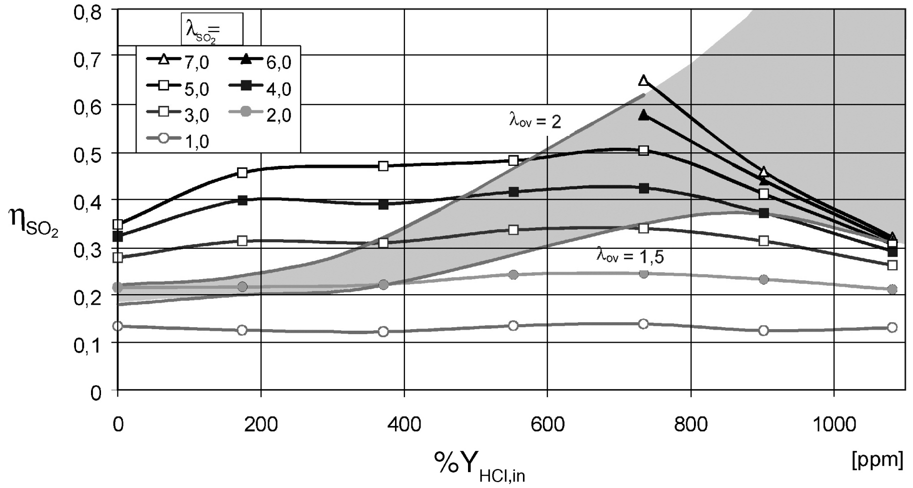

Fig. 4. Influence of HCl inlet concentration on SO_2 removal efficiency. Process parameters: $T_{in} = 225\,°C$, $\%y_{H_2O} = 0.1$, $y_{sus,Ca(OH)_2} = 10\,wt.\%$.

diffusion of $CaCl_2$). It can be seen that the overall drying rate becomes independent of the initial loading only for $y_{CaCl_2,0} > 30\,wt.\%$. This is an order of magnitude higher than the experimentally obtained value of 1.2 wt.% above which no further improvement of SO_2 absorption could be found. Therefore, the influence of the drying behavior of the $CaCl_2$ loaded droplets on SO_2 absorption cannot, by itself, explain the limitation found for higher initial $CaCl_2$ concentrations.

Skin formation and subsequent breakage of particles while examining the drying of $CaCl_2$ droplets [8]. While this is of no influence on the above estimation it may be an important factor influencing the drying process.

3.3. Simultaneous absorption of SO_2 and HCl

Fig. 4 shows the experimental results for the simultaneous absorption of SO_2 and HCl. The removal efficiency for SO_2 is depicted in relation to the HCl inlet concentration with the stoichiometric ratio for SO_2 as parameter. This representation gives an indication of what happens when HCl is added to the flue gas while all other process parameters remain constant. The marked points are interpolated from experimental data with respect to the stoichiometric ratio for SO_2. The area shaded gray indicates the stoichiometric range in which the process is operated industrially (e.g. in waste incineration plants).

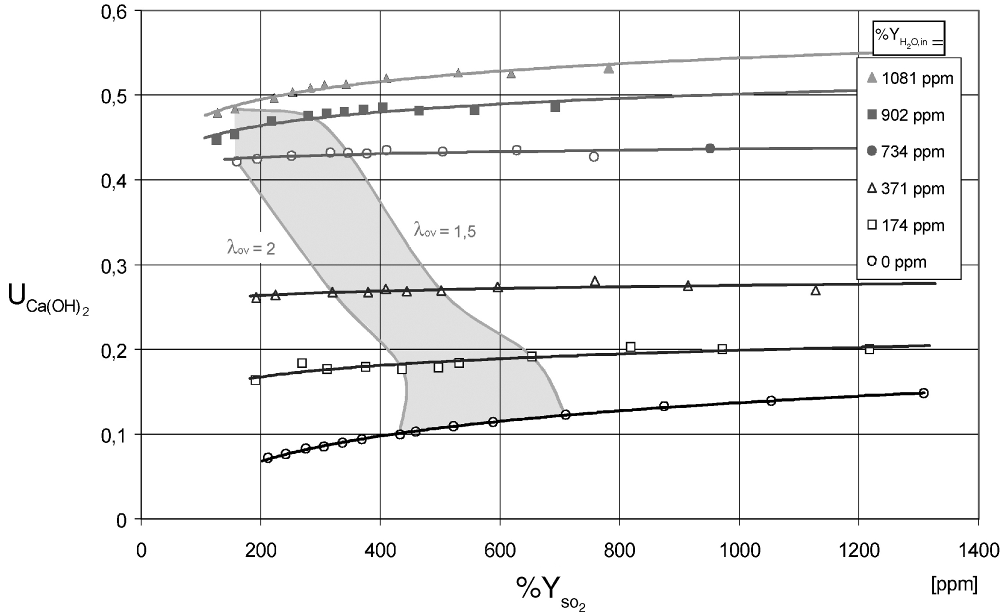

Fig. 5. Influence of SO_2 inlet concentration on $Ca(OH)_2$ conversion. Process parameters: $T_{in} = 225\,°C$, $\%y_{H_2O} = 0.1$, $y_{sus,Ca(OH)_2} = 10\,wt.\%$.

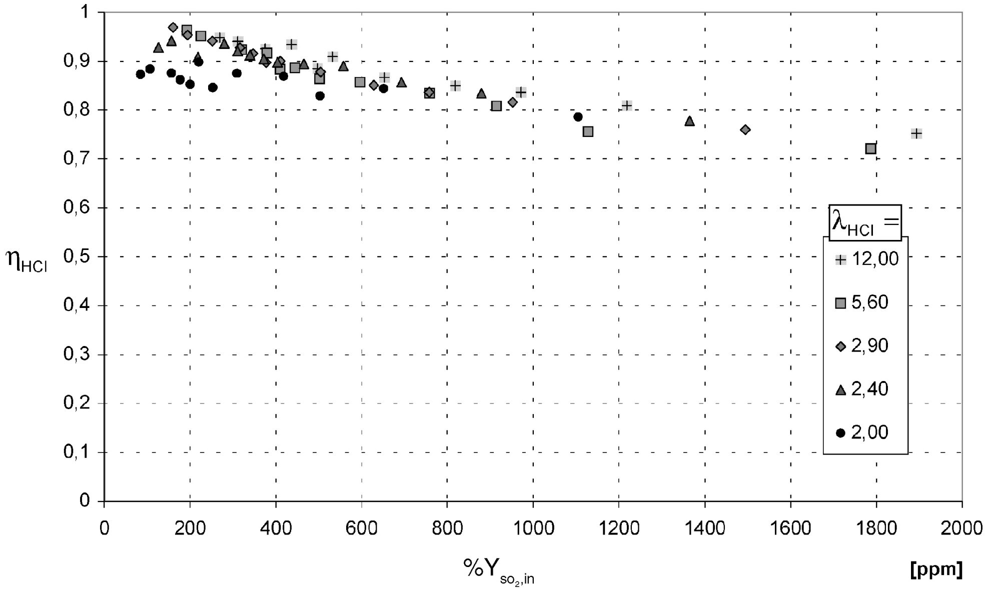

Fig. 6. Influence of SO_2 inlet concentration on HCl removal efficiency. Process parameters: $T_{in} = 225\,°C$, $\%y_{H_2O} = 0.1$, $y_{sus,Ca(OH)_2} = 10$ wt.%.

It can be seen, that at low stoichiometric ratios for SO_2, i.e. for high SO_2 concentrations, increasing the HCl concentration has no influence on SO_2 absorption. At high stoichiometric ratios for SO_2 an enhancement in SO_2 absorption is observed at low HCl concentrations. This can be interpreted as the influence of the $CaCl_2$ formed by HCl absorption.

The enhancement of η_{SO_2} for a high stoichiometric ratio of SO_2 lies in the same order of magnitude as for the case where $CaCl_2$ was added to the lime slurry. The two experiments cannot be compared directly as the results were obtained at different process parameters.

After reaching a maximum at a HCl inlet concentration of about 750 ppm the removal efficiency falls steeply with rising HCl concentration. This might be explained by taking into account, that the absorption of HCl is thermodynamically favored to the absorption of SO_2. The diffusion paths within the droplet for the sulfur components become longer as the reaction partners are taken away by the chloride. Furthermore, the dissociation reactions of the absorbed SO_2 are strongly dependent on the pH value, which in turn is lowered at the droplet surface, if the droplet absorbs HCl.

At low stoichiometric ratios for SO_2 no influence of HCl on SO_2 removal can be detected. A possible reason for this could be a conversion limitation of the $Ca(OH)_2$ with respect to SO_2 at high SO_2 concentrations. Fig. 5 shows $Ca(OH)_2$ conversion with respect to the SO_2 inlet concentration. It can be seen that the conversion of $Ca(OH)_2$ is independent of the SO_2 concentration at high SO_2 concentrations. Again, in the diagram the range of industrial relevance is shaded gray.

The removal efficiency for HCl with respect to the SO_2 inlet concentration is depicted in Fig. 6. It can be seen, that HCl is removed much more efficiently than SO_2. Only at very high SO_2 inlet concentrations, the HCl removal efficiency is slightly lowered.

In [4], the authors present some experimental results for the simultaneous absorption of SO_2 and HCl in the spray dry scrubbing process. They do not, however, vary the ratio of SO_2/HCl in their experiments. The model proposed in their paper does not take the influence of $CaCl_2$ into account.

4. Conclusions

Adding $CaCl_2$ to the lime slurry up to a mass fraction of 1.2 wt.%, enhances the SO_2 removal in spray dry absorption. This can be ascribed to the influence of $CaCl_2$ in prolonging the drying process. SO_2 absorption efficiency can, however, not be further enhanced by adding more $CaCl_2$ to the lime slurry. A rough estimation shows that the drying behavior of the salt droplets cannot solely account for this phenomena.

At low HCl concentrations in the flue gas the SO_2 absorption is enhanced, despite the fact that the net load of the droplet with acid components is increased. This can be ascribed to the influence of the $CaCl_2$ in the droplets formed by HCl absorption which again leads to a prolonged drying process.

At high HCl concentrations the SO_2 removal is lowered, which is attributed to the fact that HCl absorption and dissociation is thermodynamically favored in the competing absorption and reaction process.

Future investigations will have to clarify, how the influence of HCl on SO_2 absorption depends on the process parameters, especially the drying conditions and a model will have to be developed in order to investigate the influences of the underlying processes.

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